Response to Referee # *1*

All of the line numbers refer to Manuscript ID: amt-2020-520.

We thank the referee's valuable comments and sugestions, we response the comments points to points, revised the manuscript carefully, and polished the language throughout the manuscript. As detailed below, the referee's comments are shown as italicized font, our response is in orange, new or modified text is in blue.

The authors report on a new dissociation cavity enhanced absorption spectrometer for quantification of NO_2, RO_2NO_2 and $RONO_2$ in the atmosphere. The instrument relies on cavity-enhanced absorption spectroscopy to quantify NO_2 and NO_2 generated from organic nitrates by sampling through a heated inlet similar to what has been described by others (Thieser et al., 2016; Paul et al., 2009; Keehan et al., 2020; Chen et al., 2017; Wooldridge et al., 2010; Sadanaga et al., 2016; Di Carlo et al., 2013). Inlet characterization and sample field data are presented.

Overall, this is a well written manuscript suitable for publication for AMT after my comments below have been addressed by the authors.

Thanks for the referee's positive comments.

Major comments:

1. *Considering the large body of existing TD literature, a table comparing this new instrument to existing methods and a discussion of the differences, advantages and disadvantages should be added to the paper.*

   Thanks for the suggestion. The table comparing our instrument to existing methods and discussions were added in the revised manuscript in Section 4.2.

   As summarized in Table 2, there are several typical technologies to measure organic nitrates based on the thermal dissociation method. TD-LIF is the pioneer to determine organic nitrates by measuring NO_2 produced through pyrolysis (Day et al., 2002), and the technology has been developed well and deployed in considerable campaigns (Di Carlo et al., 2013; Farmer et al., 2006). TD-LIF has a high time resolution and low detection limit, but the determination of NO_2 has to rely on extra calibration. TD-CIMS has a similar limitation as TD-LIF, and the method can measure some individual species of PNs, which need corresponding standards to be calibrated one by one (Slusher et al., 2004). CRDS, CAPS and CEAS are all cavity-enhanced techniques with high sensitivity and time resolution, of which CRDS and CAPS have been applied to detect NO_2 after ON pyrolysis. Specifically, in this study, the ONs and PNs are determined directly through broadband absorption measurement by CEAS, which can avoid the uncertainty caused by multiple spectral fitting and subsequent differential calculations. Overall, TD-CEAS has a detection capacity similar to that of TD-LIF and others. Recently, PERCA-CRDS was developed to indirectly determine PNs by measuring NO_2 through chemical amplification, which also showed high sensitivity, but the technology for atmospheric measurements needs to be studied further.

Table 2. Typical thermal dissociation methods to measure organic nitrates.

Method	Targets	Time resolution	Detection limit	Accuracy	Reference
TD-LIF	ANs, PNs	10 s	90 pptv	10-15%	(Day et al., 2002)
TD-LIF	ANs, PNs	1 s	18.4, 28.1 pptv	22%, 34%	(Di Carlo et al., 2013)
TD-CIMS	PAN, PPN	1 s	7, 4 pptv	20%	(Slusher et al., 2004)
TD-CRDS	ANs, PNs	1 s	100 pptv	6%	(Paul et al., 2009)
TD-CAPS	PNs, ONs	2 min	7 pptv	N.A.	(Sadanaga et al., 2016)
TD-CRDS	ANs, PNs	1 s	28 pptv	6%+20 pptv	(Thieser et al., 2016)
TD-CRDS	ANs, PNs	1 s	59, 94 pptv	8%+10 pptv	(Sobanski et al., 2016)
PERCA-CRDS	PNs, PAN	1 s	6.8, 2.6 pptv	13%	(Taha et al., 2018)
TD-CEAS	ANs, PNs	6 s	90 pptv	9%	This work

Specific comments:

2. *Title - replace 'detecting' with 'measuring' or 'quantification of' (the instrument does not merely detect the presence of PN and AN after all).*

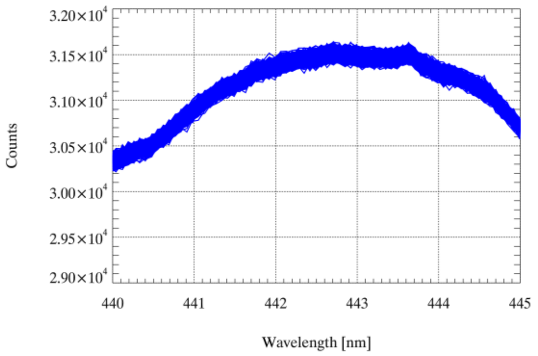
   The title is modified as: "Thermal dissociation cavity enhanced absorption spectrometer for measuring NO_2, RO_2NO_2 and $RONO_2$ in the atmosphere."

3. *line 102. Since the instrument samples through a PTFE filter, the Mie scattering component should be zero.*

   The Eq.1 is a standard euqaiton of CEAS to show the different components of the extinction coefficient. We believe there are still some particulates that can enter the cavity despite of the usage of PTFE filter, since the filter efficiency can not reach to 100%. However, the contribution of Mie scattering and Rayleigh scattering is eliminated by polynomial fitting through DOASIS.

4. *line 110. Please comment on the precision of the output power of the stabilized source.*

   The LED optical output power is about 1850 mW. We continuously measured N_2 spectral to dectect the stability of the light source. The figure shows the signal distribution of 1000 N_2 spectral, and the uncertainty of the signals is <0.5%. For example, the mean of signals at 445 nm is 30636 counts, and the 3σ is equal to 111 counts.



Line 113-115, revised as: "The core of the light source module is a single-color LED (M450D3, Thorlabs, Newton, NJ, USA), which emits more than 1850 mW optical power at approximately 450 nm with a full width at half maximum (FWHM) of 18 nm."

5. *line 119. reported by whom? ATF?*

Yes, it is. The values of reflectivity of the high-reflectivity mirror are cited from the report of ATF.

Here we revised this sentence as follow: "The reflectivity of HR mimmors (CRD450-1025-100, Advanced thin films, CO, USA) is reported by the manufacturer to be greater than 0.9999 (440 - 460 nm) with a radius curvature of 1.0 m and a diameter of 25.4 mm."

6. *line 155 please state the manufacturer and internal surface of the T-shaped solenoid valves.*

The text is revised as follows: "…, a time relay is used to periodically control the three T-shaped solenoid valves (71335SN2KVJ1, Parker Hannfin, USA), and the internal surface of the T-shaped solenoid valves is stainless steel."

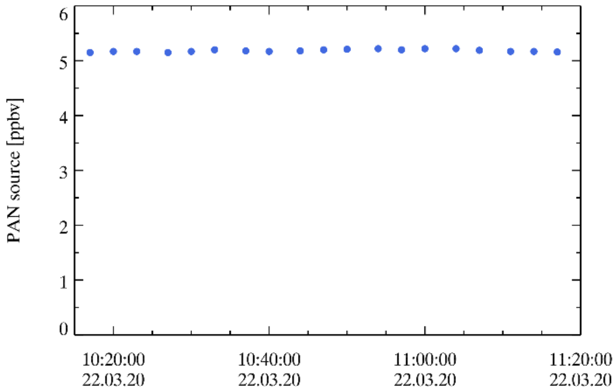
7. *line 160. Hg lamps tend to "run hot" which can affect the output of PAN, which is prone to thermal dissociation. Has the composition and purity of the PAN source been evaluated?*

Furthermore, what was the concentration or mixing ratio of acetone used?

We used a PAN source to do the experiments after the temperature of the Hg lamp in the PAN source stays stable at 39 °C, so the output of PAN source is stable. The PAN source used here is a calibration part of GC-ECD instrument, and the source level has been checked by GC-ECD. As the following figure shows, the PAN source work stably, checked by GC-ECD, with an average of 5.18 ± 0.03 ppbv. The mixing ratio of acetone standard used here is 500 ppmv.

"The source was used for the laboratory experiments after the temperature of the

Hg lamp stablised at 39.0 °C, and the source level and stability were double-checked by a GC-ECD instrument.”



8. *line 166 which requirements?*

   The requirements refer to the need to use some typical mixing ratio of NO_2/NO during instrument characterization and interference correction, so the text is revised as follows: “…, and outputted well-mixed gases by diluting NO or NO_2 with zero air according to the requirement of studying the potential interference caused by ambient NO and NO_2.”

9. *line 182. Please describe how N_2 and He were delivered (sampled from the tip of the inlet, or statically).*

   N_2 and He were delivered through the purge flow injection lines, so the text is revised as follows: “The spectra of pure N_2 (>0.99999) or He (>0.99999) filling the cavity through the purge lines, are collected to calibrate the mirror reflectivity, …”

10. *line 226. Please justify omitting glyoxal from the fit and estimate the uncertainty introduced. Figure 4 suggests that the contribution of glyoxal was small but that may not always be the case. What (if anything) happens to the NO_2 retrieval when glyoxal is included in the fit?*

    We agree with that the including of glyoxal retrieval would affect the determination of NO_2. We compare the two cases with and without the glyoxal retrieval during the spectral fitting. The comparison shows the inclusion of glyoxal bring bigger fitting residual, which is consistent with the result of recent study (Liu et al., 2019). While the difference of retrived NO_2 concentration between the two fitting method is small. As shown in the following figure, the relative difference of derived NO_2 concentration suggests the uncertainty by omitting σ(glyoxal) from spectral fitting is about 4%.

    Line 240 revised as: “…but here, we do not take glyoxal absorption into consideration in spectal fiting. The inclusion of glyoxal in the spectral fitting would enlarge the fitting residual. Our field measurement showed that the uncertainty caused by excluding glyoxal fitting was approximately 4% (Fig. S2)."

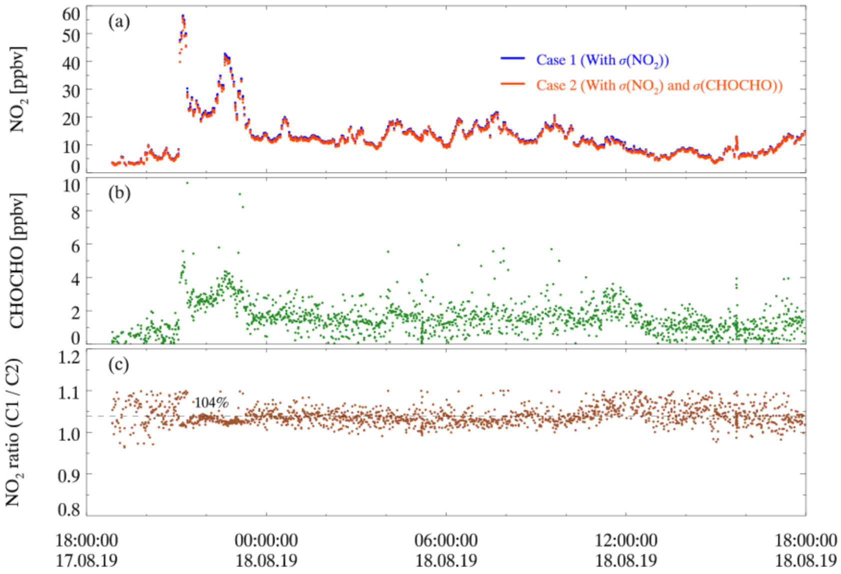
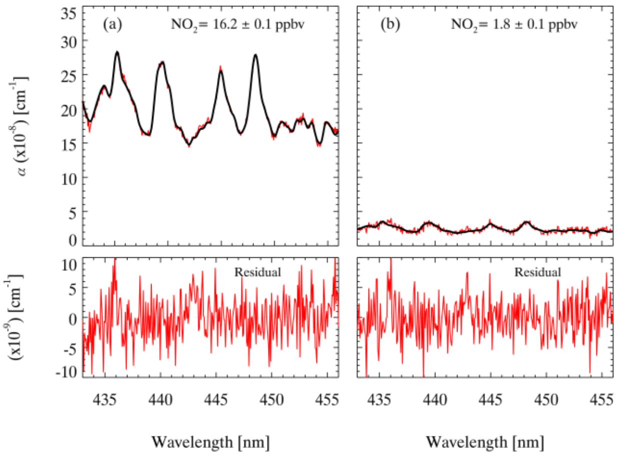


Figure S2. An example of the comparison about the fitting results with considering the cross section of glyoxal or without. Panels show the case on August 17, 2019 and August 18, 2019 during CHOOSE campaign. Panel (a) shows the time series of NO_2 under two different conditions. Panel (b) shows the time serie of glyoxal under Case 2. Panel (c) shows the concentration ratio of NO_2 under two different cases.

11. *line 236 - Figure 4. Please state the uncertainty of the NO_2 mixing ratios (16.2±? ppbv).*

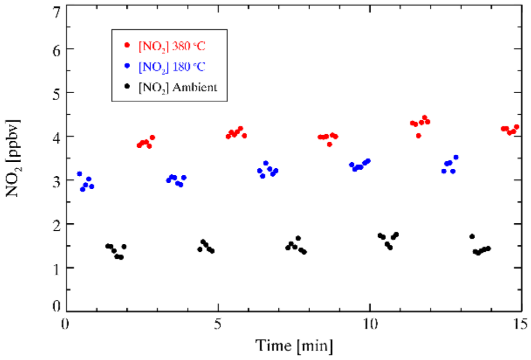
    The uncertainty caused by the residual of spectral fitting are added in Figure 4 (16.2 ± 0.1 ppbv, 1.8 ± 0.1 ppbv), and revised accordingly in the manuscript.



12. *line 240 - Figure 5. It seems that the timing of the inlet temperature switch was off*

as there are blue data points at the same level as [NO_2]ambient and red data points at the same level as 180 °C.

As the Figure 5 shows, a measurement cycle includes 3 phases whose furation is 60 s, but the CEAS may still detect the air flow from previous channel when the measurement phases just switch. Here we excluded the transition point of each phases and the two data points before and after the transition point to avoid the misundetstanding. The Figure 5 is revised as follow.



13. *lien 248 It is 1 spectrum, but the plural should be 2 spectra (not "spectrums").*
    Corrected accordingly.

14. *line 283. An alternative (and more likely) interpretation of the second plateau is the presence of alkyl nitrate impurity. What are the operating temperature and the output purity of the photochemical PAN source? Is [PAN]out = [NOx]in ?*
    Thank you for the comment. The operature temperature of photochemical PAN source stays 39 °C, and [PAN]out equals to 92 ± 3% of [NOx]in.
    The presence of alkyl nitrates in PAN source was once reported by previous reports (Paul et al., 2009). In this study, we can not ruled out the possibility of the alkyl nitrate impurity. But the fact that the source of [PAN]out is equal to 92 ± 3% of [NOx]in, suggesting that only a very small percentage (≤ 8% on average), if any, of the ANs. Futhermore, Figure 7 demonstated that the second plateau can be well explained by recombination of NO_2 with RO_2, and Figure 8 showed the concentration of PAN source and wall loss rate of RO_2 affect the presence of the second plateau, so it is reasonable of our explatation that attribute the formation of the second plateau to recombination reaction of PAN.
    In the revised manuscript, we added the following sentences to discuss the possibility of ANs impurity to the dissociation profile of PNs.
    Line 294: "approximately 400 °C (Friedrich et al., 2020). The presence of alkyl nitrates in PAN source has been reported before by previous studies, and was regarded as the reason of the dual-plateau profile of PNs dissociation (Paul et al.,

2009). Here, we cannot ruled out the possibility of alkyl nitrate impurities. However, the source level of PAN is equal to 92 ± 3% of NOx imput, which suggests that only a very small percentage (≲ 8% on average), if any, of the ANs."

15. *lines 283-284. The PAN dissociation temperature of 400 °C reported by Friedrich et al. is an outlier and inconsistent with every other paper on this subject. At a residence time of 142 ms (line 153) and using rate constant for unimolecular decomposition reported by (Kabir et al., 2014), PAN is predicted to be 99% dissociated at a temperature of "only" 127 °C.*

    We agree with the comment. As our model result shown in the following figure, PAN is well thermally dissociated to NO_2 at 180 °C in the heated tube, but the recombination of PAN not only occurrs at heated part but also at the subsquent cooling part in the heated channel. The overall dissociation temperature of PAN depends not only on the concentration of PAN source and the wall loss rate of RO_2, but also on the settings of the instrument. The line 285-287 is revised as follows: "…If the PAN source is equal to 4 ppbv in the PNs channel at 180 °C, as Fig. S3 shows, PAN will first be dissociated completely, and then the PA will recombine with NO_2 to form PAN when the air flow passes the cooling lines."

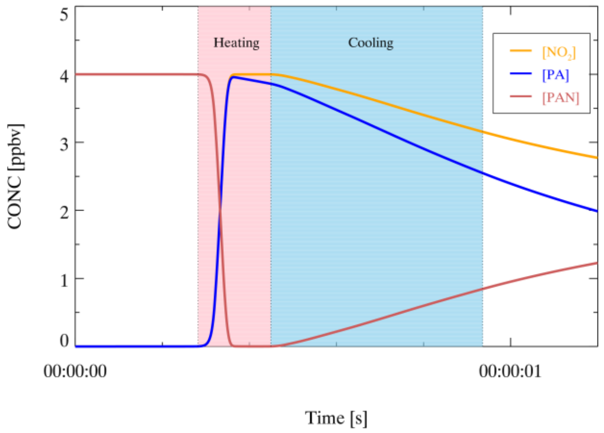


Figure S3. A simulated example of the PAN pyrolysis in the PNs channel at 180 °C if the PAN source is equal to 4 ppbv. The concentration of relative species changes with the residence time, the red line is concentration of PAN, the blue line is the concentration of PA radical, and the yellow line is the concentration of NO_2. The red part in the plot is the duration time when the air flow goes through the heating part of quartz tube, and the blue part is the duration time when the air flow goes through the cooling part.

16. *line 286 - how much time is there for recombination to occur?*

    According to the simulation results of the box model, when the setting temperature is 180 °C， the duration time for the recombination to occur after the heated tube to the detector is 297 ms.

17. *line 290. $CH_3O_2NO_2$ more readily dissociates than PAN; under the conditions of the authors' inlet, it is predicted to be >99% dissociated at a temperature of <50 °C.*

    Yes, $CH_3O_2NO_2$ more readily dissociates than PAN, but $CH_3O_2NO_2$ is one of the derivative products during the thermal dissociation of PAN. As Figure 7 shows, the presence of $CH_3O_2NO_2$ only occurs at pretty high temperature, and $CH_3O_2NO_2$ comes from the following two reasons. Firstly, the temperature first rises and then falls in the heated tube and the subsequent cooling lines, so PAN in the air flow tend to dissociate and then falling temperature promotes some other reactions, like the recombination of PAN. Secondly, the dissociation of PA accelerates in the heated channel with the temperature increasing. Therefore there are some CH_3O_2 as a product of the disscaition of PA, which is likely to react with NO_2 to produce a small amount of $CH_3O_2NO_2$ at the cooling part.

18. *line 291. The two plateaus can also be interpreted as a ~2:1 mixture of PAN and alkyl nitrates - can this be ruled out (see question for lines 160 and 283).*

    Please attach the Comment and Response #13. In order to clarify the problem, other instruments which is able to measure the individual species of ONs, may be useful to test the purify of the PAN source in the future.

19. *line 294. Please state how much time there is for recombination to occur.*

    As mentioned in comment 15, when the setting temperature is 180 °C, the duration time for the recombination to occur is 297 ms. The text is revised as follows: "The first plateau at 180 °C is caused by the recombination of PA and NO_2 after the pyrolysis of PAN, and the time for recombination from the end of the tube to the detector is 297 ms. "

20. *line 318 Caption to Figure 7 - are gray/green and PAN/NO_2 backwards?*

    NO. As Figure 7 shows, the gray columns represent undissociated or recombinated PAN. Similarly, the green columns represent NO_2 thermal dissociated from PAN source.

21. *line 326 Filter and wall losses are small only if they the filter and wall material are made from Teflon. Please rephrase.*

    Yes, the text is revised as follows: "Previous studies have shown that the filter losses and wall losses of NO_2, PNs and ANs are small when using Teflon tubes and Teflon filters (Paul et al., 2009; Thieser et al., 2016)."

22. *The statement is true for ANs such as methyl or ethyl nitrate; not sure the statement is true for isoprene nitrates that are prone to hydrolysis (Vasquez et al., 2020).*

This is a good question. Once formed, isoprene nitrates are prone to incorporate into aerosol where the hydrolysis of isoprene nitrates will happen. This is a vital problem for the sampling of isoprene nitrates. We do not evaluate the sampling loss of the isoprene nitrates. The wall loss is likely to be reduced if the frequency of filter changing is improved.

23. *line 426 Replace MeN with Methyl nitrate (one is not supposed to start a sentence with an abbreviation or acronym).*

    Corrected accordingly.

24. *line 448. It is worthwhile noting that these molecules are important only at night and early morning hours - for this reason, the Cohen group has generally not reported AN data at those times of day.*

    Please cite (Thaler et al., 2011) for $ClNO_2$ *and (Womack et al., 2017) for* N_2O_5*.*

    The text has changed as : "In addition to the interference mentioned above, other nitrogen compounds may undergo pyrolysis to generate NO_2 in the heated channels, such as N_2O_5 and $ClNO_2$ (Li et al., 2018; Thaler et al., 2011; Wang et al., 2017a; Womack et al., 2017), which may be a source of uncertainty for measurements of organic nitrates at night and early morning. Interferences can be extracted if the simultaneous measurement of N_2O_5 and $ClNO_2$ are available."

25. *line 462/465. It is 1 spectrum, and 2 spectra (not "spectrums").*

    Corrected accordingly.

26. *line 465 "as shown in Fig. 9a. The 21077 spectrums" Figure 9a does not show this information (11a perhaps?). What is meant by 21077?*

    Thank you for the correction. Line 465 "as shown in Fig. 9a. The 20177 spectrums" should be "as shown in Fig. 11(a). The 20177 N_2 spectra". The 21077 is the number of spectra applied to calculate Allan variance and LOD of the instrument.

27. *line 467 Fig. 9b should be 11b.*

    Corrected accordingly.

28. *line 500 "up to 0.99" - please state the actual value of r*

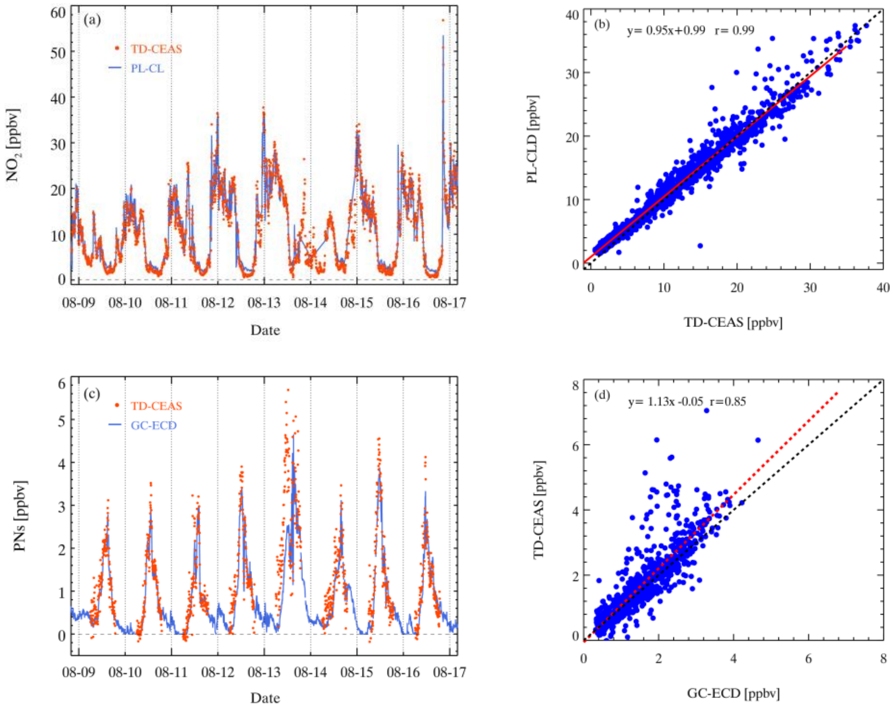
    The text is revised as follows: "Fig. 13(b) shows that the correlation coefficient of the NO_2 concentration measured by the two instruments is 0.99."

29. *line 514 Figure 13. I am not sure what is plotted here. The GC-ECD data are labeled "PAN" on the left-hand side, but PNs on the right-hand side. Tthe TD-CEAS*

data are labeled PNs on the left but PAN on the right.

In principle, the GC-ECD can observe PAN, PPN etc. and those can be summed to ΣPN. Was this done?

Thank you for the correction, there was a label mistake. We corrected and replot it as follows.



References.

Day, D. A., Wooldridge, P. J., Dillon, M. B., Thornton, J. A., and Cohen, R. C.: A thermal dissociation laser-induced fluorescence instrument for in situ detection of NO2, peroxy nitrates, alkyl nitrates, and HNO3, J. Geophys. Res.-Atmos., 107, 2002.

Di Carlo, P., Aruffo, E., Busilacchio, M., Giammaria, F., Dari-Salisburgo, C., Biancofiore, F., Visconti, G., Lee, J., Moller, S., Reeves, C. E., Bauguitte, S., Forster, G., Jones, R. L., and Ouyang, B.: Aircraft based four-channel thermal dissociation laser induced fluorescence instrument for simultaneous measurements of NO2, total peroxy nitrate, total alkyl nitrate, and HNO3, Atmos. Meas. Tech., 6, 971-980, 2013.

Friedrich, N., Tadic, I., Schuladen, J., Brooks, J., Darbyshire, E., Drewnick, F., Fischer, H., Lelieveld, J., and Crowley, J. N.: Measurement of NOx and NOy with a thermal dissociation cavity ring-down spectrometer (TD-CRDS): instrument characterisation and first deployment, Atmos. Meas. Tech., 13, 5739-5761, 2020.

Liu, J., Li, X., Yang, Y., Wang, H., Wu, Y., Lu, X., Chen, M., Hu, J., Fan, X., Zeng, L., and Zhang, Y.: An IBBCEAS system for atmospheric measurements of glyoxal and methylglyoxal in the presence of high NO2 concentrations, Atmos. Meas. Tech., 12, 4439-4453, 2019.

Paul, D., Furgeson, A., and Osthoff, H. D.: Measurements of total peroxy and alkyl nitrate abundances in laboratory-generated gas samples by thermal dissociation cavity ring-down spectroscopy, Rev. Sci. Instrum., 80, 2009.

Sadanaga, Y., Takaji, R., Ishiyama, A., Nakajima, K., Matsuki, A., and Bandow, H.: Thermal dissociation cavity attenuated phase shift spectroscopy for continuous measurement of total peroxy and organic nitrates in the clean atmosphere, Rev. Sci. Instrum., 87, 2016.

Slusher, D. L., Huey, L. G., Tanner, D. J., Flocke, F. M., and Roberts, J. M.: A thermal dissociation-chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide, J. Geophys. Res.-Atmos., 109, 2004.

Sobanski, N., Schuladen, J., Schuster, G., Lelieveld, J., and Crowley, J. N.: A five-channel cavity ring-down spectrometer for the detection of NO2, NO3, N2O5, total peroxy nitrates and total alkyl nitrates, Atmos. Meas. Tech., 9, 5103-5118, 2016.

Taha, Y. M., Saowapon, M. T., Assad, F. V., Ye, C. Z., Chen, X. N., Garner, N. M., and Osthoff, H. D.: Quantification of peroxynitric acid and peroxyacyl nitrates using an ethane-based thermal dissociation peroxy radical chemical amplification cavity ring-down spectrometer, Atmos. Meas. Tech., 11, 4109-4127, 2018.

Thieser, J., Schuster, G., Schuladen, J., Phillips, G. J., Reiffs, A., Parchatka, U., Pohler, D., Lelieveld, J., and Crowley, J. N.: A two-channel thermal dissociation cavity ring-down spectrometer for the detection of ambient NO2, RO2NO2 and RONO2, Atmos. Meas. Tech., 9, 553-576, 2016.